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Diameter-controlled growth of aligned single-walled carbon nanotubes on quartz using molecular nanoclusters as catalyst precursors

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Molecular nanoclusters containing Fe and Mo atoms have been used as catalyst precursors for the growth of single-walled carbon nanotubes (SWNTs) on stable temperature (ST)-cut quartz substrates by chemical vapor deposition. Attribute to the uniform catalyst nanoparticles and the confinement effect of the crystalline substrates, well-aligned SWNTs with narrow diameter distribution have been synthesized. Atomic force microscopy measurements show that the mean diameter of the nanotubes obtained by thermal decomposition of ethanol at 900°C is 0.76 ± 0.16 nm, which is the smallest among all reported results for aligned SWNTs. The mean diameter of the nanotubes increases with growth temperature. In addition to using identical nanoclusters as the catalyst precursors, the avoidance of annealing treatment of catalyst precursors is also a key point for obtaining SWNTs with controlled diameters. Using these identical nanoclusters as catalyst precursors and carefully tuning the growth parameters make us closer to the ultimate goal of controlling the chirality of SWNTs.

molecular nanoclusters, single-walled carbon nanotubes, diameter control, quartz, catalysts

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Single-walled carbon nanotubes (SWNTs) have attracted intensive attention for their potential applications in many fields especially in carbon-based nanoelectronics [1]. Though it has been shown that individual SWNT field-effect transistor (FET) achieves good performance [2–4], it still remains a big challenge to integrate them into large-area circuits for the next generation electronic devices. Providing SWNTs with designed structure, orientation, and position is essential in this evolvement for the success of carbon-nanotube-based electronics. Chemical vapor deposition (CVD) seems a promising method for the direct growth of SWNTs on substrates which are immediately ready for building devices [5]. The direct growth processes prevent SWNTs from being damaged and contaminated, which are inevitable during the purification and dispersing treatment of the bulk-form SWNTs [6].

It is normally accepted that SWNTs are grown via vapor-liquid-solid (VLS) mechanism. Although the orientation of SWNTs can be regulated by adjusting the direction of the gas flow [7–9], or by the surface lattice of the single crystal substrates such as sapphire and quartz [10–14], the structure control of SWNTs is still a big challenge. Diameter control is the first step toward structure control. In the VLS growth process, the SWNTs are nucleated on catalyst nanoparticles. Therefore, the diameter and structure are highly dependent on the size and property of the catalyst nanoparticles. However, since the widely used metal catalysts such as Fe, Co, Ni, and Cu normally form nanoparticles by reducing their inorganic salt precursors deposited on the substrates, it is difficult to obtain uniform metal nanoparticles to initiate the

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SWNT formation and consequently to control the diameter of SWNTs [15–18]. Using preformed uniform nanoparticles as catalysts [19] or using dendrimer and copolymer micelles to confine the size of catalyst precursor particles [20,21] can improve the diameter distribution of the produced SWNTs. A more accurate control on the size of the catalyst nanoparticles has been realized by using ferritin to load certain amount of iron atoms in each ferritin cage [22]. However, it is too expensive to use ferritin in large quantity as consumables. A more interesting strategy is to use inorganic molecular clusters based on transition metals as catalyst precursors. These clusters have identical molecular structure [23] and hence are able to form very uniform catalyst particles. An et al. [24] first used molecular nanoclusters $[H_x\text{-}PMo_{12}O_{40} \subset H_4MoV^{I}_{72}Fe^{III}_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}]\cdot 60H_2O$ as catalyst precursor to grow random SWNTs on silicon substrates. The mean diameter of the resultant SWNTs was 1.0 nm with a standard deviation of 17% at the optimized condition. The diameter distribution was broader when the nanoclusters were not well dispersed on the substrates. The aligned SWNT arrays are more attractive than random SWNT networks for the application in nanoelectronics. It was reported that the surface lattice of the crystalline substrates may introduce a confinement to the diameter of grown SWNTs [25]. Therefore it is of interest to study the growth of SWNT arrays on crystalline substrates using molecular nanoclusters as catalyst precursors and find out how the diameter of SWNTs is modulated cooperatively by the catalyst particles and the surface lattice of the substrates and to what extent we can manipulate the diameters of the SWNTs in an array. This will help us to develop strategies to realize the exact and flexible control on the diameter of SWNTs.

1 Experimental

1.1 Synthesis of catalyst precursors

The molecular cluster $[H_x\text{-}PMo_{12}O_{40} \subset H_4MoV^{I}_{72}Fe^{III}_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}]\cdot 60H_2O$ was synthesized using the pathway reported by Müller et al. [23] and carefully characterized with the methods therein.

1.2 Chemical vapor deposition

Stable temperature (ST)-cut single crystal quartz was used as the substrate for the SWNT growth. The catalyst precursors were dissolved in the mixed solvent of 80% ethanol and 20% water. After dropping the catalyst precursor solution onto the substrate and drying in ambient atmosphere, the substrate was placed into the quartz tube reactor. The substrate was at first heated to 900–970°C in 200 standard-state cubic centimeters per minute (sccm) of H_2, and then ethanol was bubbled into the reactor with 100 sccm of H_2 for 15 min to grow SWNTs. Finally, it was cooled down to room temperature under Ar flow.

1.3 Characterization

Scanning electron microscopy (SEM, Nova Nano 430, FEI, Japan) was operated at 1 kV. Raman spectra were collected on a Jobin Yvon LabRam Aramis micro-Raman spectrometer with excitation wavelength of 632.8 or 532 nm with a spot size of 1 μm, using a 100× air objective. The laser energy was carefully controlled to avoid any heat effect. SWNTs grown on quartz were transferred to silicon substrates using PMMA for Raman measurements [26]. Atomic force microscopy (AFM, Veeco diMutiMode V, operated at tapping-mode) was used to measure the diameter of the SWNTs and the size of the catalyst particles. The XPS data were collected in an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, binding energies were calibrated using C1s hydrocarbon peak at 284.8 eV.

2 Results and discussion

Figure 1(a)–(d) show the scanning electron microscopy (SEM) images of SWNTs grown on quartz substrates at different growth temperatures using Fe-Mo nanoclusters as catalyst precursors. The oxidation of molybdenum may change the size and composition of the nanoparticles because the molybdenum oxides sublimate at 600ºC. In order to avoid the formation of volatile molybdenum oxides, the CVD system was purged under H_2 atmosphere before the carbon stocks was added. H_2 treatment also reduced the nanoclusters to metallic nanoparticles, which then acted as the catalysts to initiate the growth of SWNTs after ethanol was bubbled into the reactor. In Figure 1(a)–(d) it can be found that the grown tubes were all aligned along certain direction. The density of SWNTs was quite low at 900 ºC. When the growth temperature was increased to 920 and 940ºC, the tube density was dramatically increased. When the temperature was further increased to 970ºC, the tube density was slightly reduced. We measured the diameters of the SWNTs from the atomic force microscopy (AFM) height profiles [27]. Figure 1(e) shows a typical AFM image of SWNTs grown at 920°C. From the cross section analysis, the diameters of the four SWNTs in the image are all below 1.0 nm.

Besides the tube density, the diameter distributions of the SWNTs grown at different temperatures are also varied. We measured the diameters of the SWNTs using AFM and the statistical results are shown in Figure 2. For SWNTs grown at 900°C, the diameter of the SWNTs is quite uniform. We measured altogether 23 tubes on several different samples

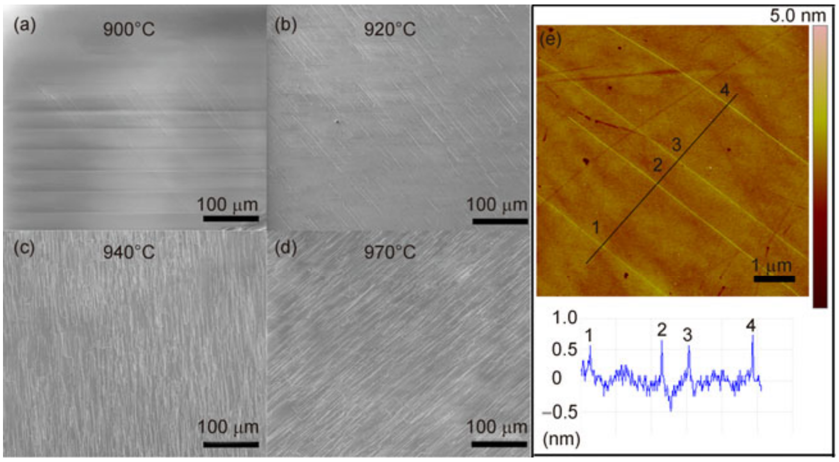

Figure 1 (a)–(d) SEM images of SWNTs grown at different temperatures by using molecular Fe-Mo nanoclusters as catalyst precursors, (a) 900°C, (b) 920°C, (c) 940°C, (d) 970°C. (e) AFM image and the height profile of the SWNTs grown at 920°C.

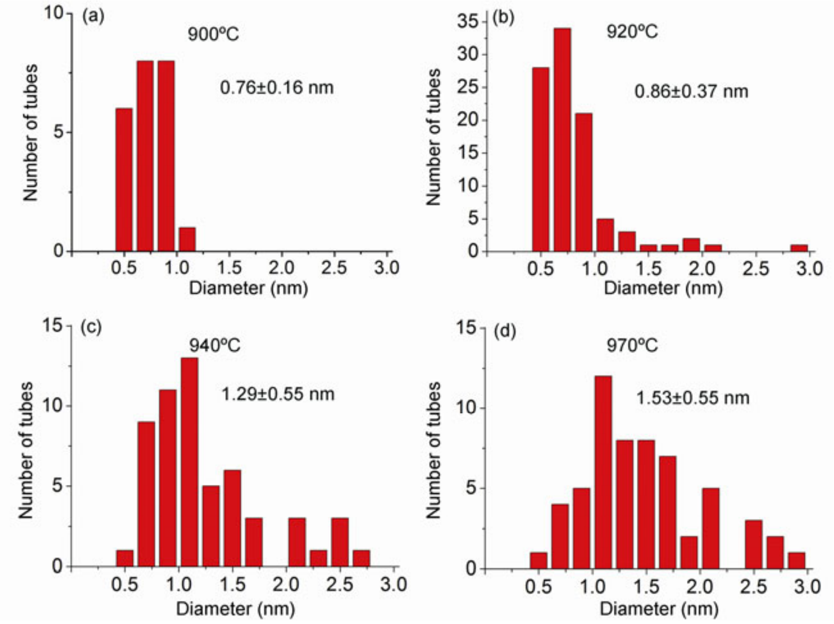

Figure 2 Diameter distributions of SWNTs obtained at different growth temperatures using molecular Fe-Mo nanoclusters as catalyst precursors. (a) 900°C, (b) 920°C, (c) 940°C, (d) 970°C.

grown at 900ºC. More than 95% (22 of 23 tubes) of the SWNTs have diameters below 1.0 nm, with a mean diameter of 0.76 nm and a standard deviation of 0.16 nm (Figure 2(a)). For SWNTs grown at 920°C, the mean diameter went up to 0.86 nm while the diameter distribution is still very narrow. The 86% (84 of 98 tubes) of the SWNTs have diameters below 1.0 nm (Figure 2(b)). For SWNTs grown at higher temperatures (940 and 970°C), the mean diameter increased to 1.29 nm and 1.53 nm respectively and the diameter distribution were also broader (Figure 2(c) and (d)).

The temperature effect on the nanotube diameter was further verified by Raman spectra. Figure 3 shows the radical breathing modes (RBM) of resonance Raman spectra for SWNTs grown at different temperatures. The RBM frequency has been proven to be dependent on the diameter d_t following the relation $\omega_{\mathrm{RBM}}=a/d_t+b$, where a and b are empirically derived parameters [28]. Individual SWNTs can only be detected by resonant Raman signals when their electronic transition energies match well with the laser energy. Small diameter SWNTs have a small variety of (n, m) types and a large variation in their transition energies, which means they are more difficult to be detected than the large diameter SWNTs when using only a few laser excitation energies in the Raman experiment [29]. Because quartz substrate was not friendly to Raman characterization, the SWNTs was transferred onto SiO_2/Si substrates using the peel-off method [26]. The RBM band shown in Figure 3(a) corresponds to a (7,6) SWNT with the diameter of 0.895 nm.

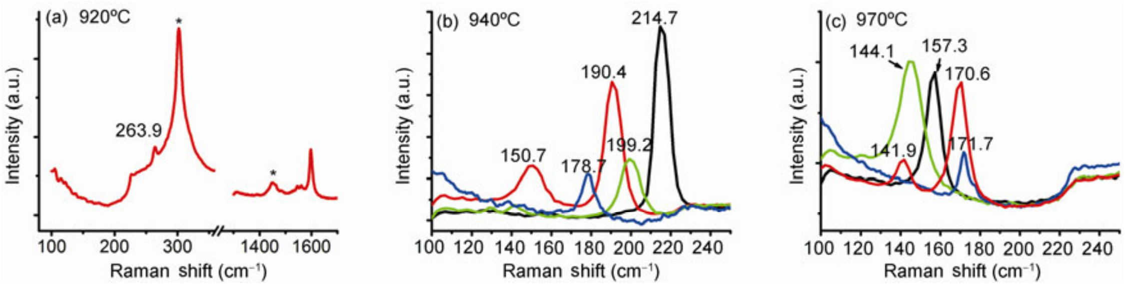

Figure 3 Raman spectra of SWNTs grown by using molecular Fe-Mo nanoclusters as catalyst precursors at different temperatures, (a) 920°C, (b) 940°C, (c) 970°C. The peaks marked with stars correspond to the Raman spectra of the silicon substrates. The Raman spectrum in (a) was recorded with an excitation laser line of 632.8 nm, spectra in (b),(c) were recorded with an excitation laser line of 532 nm.

The weak intensity of the D-band shows the high-quality of the small diameter SWNT. This sample was grown at 920°C. From Figure 3(b) and (c), RBM bands shift to lower frequencies, indicating that the diameters increased with growth temperature. This result is in good accordance with the AFM measurements.

The above results show that we can manipulate the diameters of SWNTs grown on quartz by varying the growth temperature. What's more interesting is that we are able to obtain aligned SWNTs of very small diameter and with very narrow distribution. In previous reports, the mean diameter of SWNTs grown on quartz with Fe catalysts is usually ranged from 1.2 to 1.7 nm [11,14,25,30]. The diameters of aligned tubes grown on silicon wafers oriented by gas flow are from 0.9 to 3.3 nm with a mean value of 2.0 nm [8]. The average diameter of tubes we obtained at 900 and 920°C are 0.76 and 0.86 nm, respectively. This indicates that using molecular nanoclusters as catalyst precursors plays an important role in obtaining smaller and uniform SWNTs. It is of great interest that the average diameter of random SWNTs grown at 900°C on silicon substrates also using Fe-Mo clusters as catalyst precursors is ~1.0 nm [24], in comparison with ~0.76 nm for tubes we obtained on quartz wafers. Ding et al. [25] showed that the surface lattice of quartz substrates could constrain the diameter of the SWNTs and lead to a narrower diameter distribution. Therefore, it is reasonable to assume that the quartz substrates contribute to the further reduction in the tube diameters.

As stated previously, it is widely accepted that the diameters of the produced SWNTs are determined by the size of the catalyst nanoparticles according to the VLS mechanism [5]. Though the Fe-Mo nanoclusters have a well-defined structure and each of the nanoclusters has identical size, they tend to aggregate when deposited onto the substrate and during the growth process. In order to reduce the aggregation, the concentration of the nanocluster solution we used was below 10^{-6} mol/L. The surface property of substrates is another important issue. The substrates should be hydrophilic to ensure the uniform distribution of the catalyst precursor solution. They also should have affinity to the nanoclusters in order to fix the nanoclusters and weaken the tendency of aggregation. After treated in Piranha solution, the quartz wafers are hydrophilic and affinitive enough. No surface modification [24] is needed.

In most CVD processes, the catalyst precursors were annealed in air and then reduced into metal nanoparticles. In An's work, they annealed the Fe-Mo nanoclusters in air at 700°C to decompose the organic ligands of the molecular clusters. However, MoO_3 can be sublimed at 600°C. Thus the annealing process may cause the loss of molybdenum [31]. X-ray photoelectron spectroscopy (XPS) analysis in Table 1 shows that the molar ratio of Fe/Mo is 1∶1.14 prior to annealing. After annealed in air at 700°C and then reduced at 920°C, the Fe/Mo ratio is 1∶0.42. If the reactor was purged under H_2 atmosphere from the very beginning of the heating process till 920°C, the Fe/Mo ratio is 1∶1.25. The proportion of molybdenum was dramatically decreased after annealing in air but was slightly increased if protected by H_2. The decrease is obviously due to the sublimation of MoO_3 while the increase may be owing to the evaporation of metallic iron, which has a much higher vapor pressure than molybdenum at 920°C.

Figure 4 shows the SEM image and the diameter distribution of SWNTs grown with the catalysts obtained from the nanoclusters annealed in air at 700°C and then reduced at 920°C. The diameters of the SWNTs range from 0.6 to 2.8 nm with a mean value of 1.33 nm. The average diameter is larger and the distribution is broader than the SWNTs obtained at the same growth temperature from the nanoclusters without annealing in air. The annealing process may increase the transference of substances on the substrates

Table 1 Molar ratio of Fe/Mo determined by XPS in different conditions [a)]

Condition	Fe:Mo
a	1∶1.14
b	1∶1.25
c	1∶0.42
d	1∶1.20

a) Condition a, the original nanoclusters. Condition b, the nanoclusters under H_2 protection from room temperature till 920°C. Condition c, the nanoclusters annealed in air at 700°C and then reduced at 920°C. Condition d, the mixture of metal salts under H_2 protection from room temperature till 920°C.

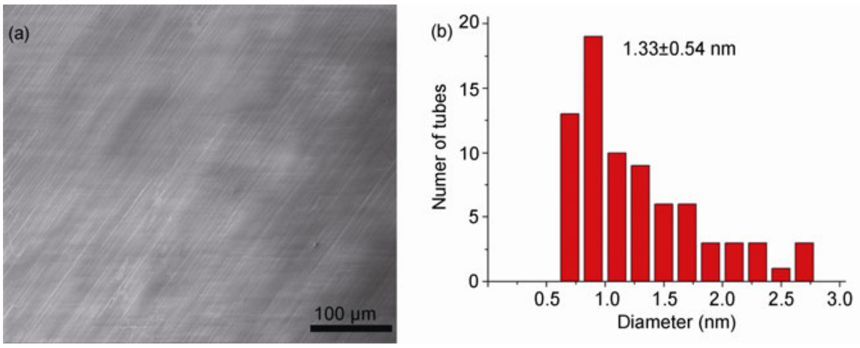

Figure 4 SEM image (a) and diameter distribution (b) of SWNTs prepared at 920°C using molecular Fe-Mo nanoclusters annealed in air at 700°C as catalyst precursors.

and the aggregation of nanoparticles therefore result in larger nanoparticles with a wider size distribution. The sublimation of MoO_3 may further aggravate such tendency. This was revealed by the data in Figures 5(a)–(d). The sizes of the particles were obtained from the heights of the features in the AFM images. As shown in Figure 5(a), when the nanoclusters were annealed in air at 700°C before being reduced at 920°C, the resultant Fe-Mo nanoparticles are obviously not uniform. The mean size of the particles is 4.41 nm with a broad size distribution of 1.49 nm (Figure 5(b)). When the treatment was under H_2 atmosphere from room temperature to the reduction temperature of 920°C, the mean size of the catalyst particles is 0.73 nm with a standard deviation of 0.21 nm (Figure 5(d)). Therefore, annealing of catalyst precursors is not favorable for obtaining uniform catalyst nanoparticles and consequently unfavorable for producing SWNTs of narrow diameter distribution.

For the samples treated at 940 and 970°C under H_2 atmosphere without annealing in air, the mean particle sizes increased to 0.78 and 1.28 nm, respectively, and the diameter distributions are also broader (Figure 5(f) and (h)). It is found that the size of the Fe-Mo nanoparticles increases with temperature and so does the size distribution. It is obvious that this tendency agrees with that of the SWNT diameters. But the average diameters of the produced SWNTs are larger than those of the nanoparticles. There are at least three possible reasons. First, small nanoparticles are not stable during the CVD process at high temperature. They tend to vanish by evaporation or grow into larger particles through an Ostwald ripening process. Second, the smaller particles are poisoned by the superfluous carbon feeding [32]. Third, the diameter of the nanoparticle is increased due to the carbon dissolution and hence the resultant SWNT has a larger diameter than the original catalyst particle.

Comparison between the diameters of produced SWNTs and the sizes of the Fe-Mo nanoparticles obtained from the Fe-Mo molecular nanoclusters reveals that the diameter of SWNTs are determined by the size of the catalyst nanoparticles. In order to further verify that using such identical Fe-Mo nanoclusters is the crucial reason to control the diameter of the SWNTs grown on quartz, we designed a

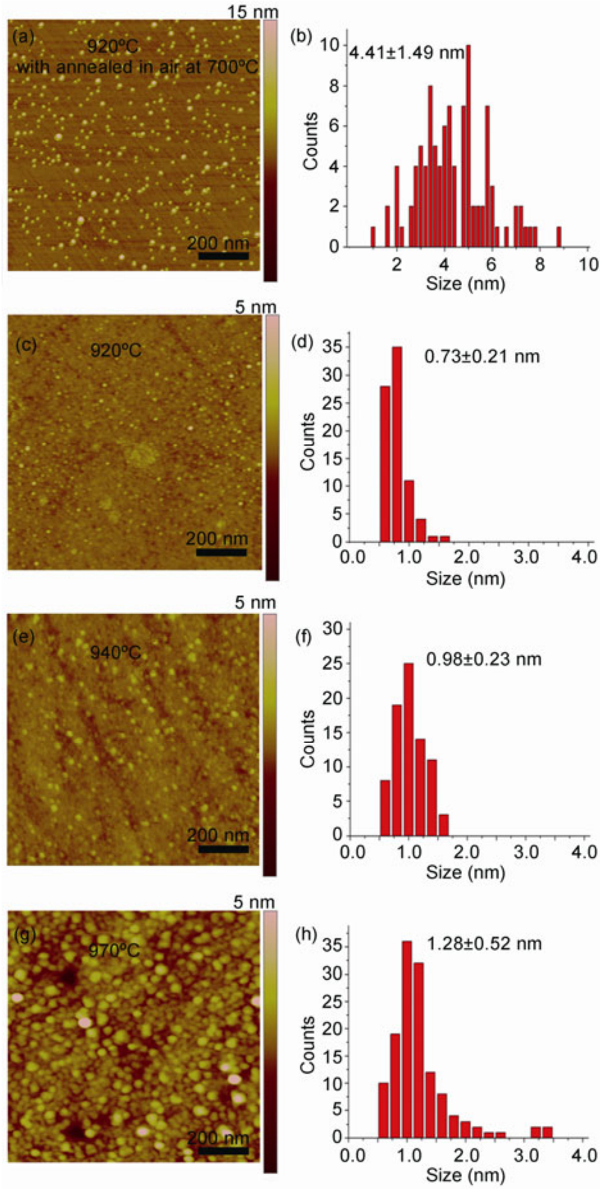

Figure 5 AFM images((a), (c), (e), (g)) and size distributions ((b), (d), (f), (h)) of molecular Fe-Mo nanoclusters after H_2 reduction at various temperatures with or without annealing in air at 700°C before reduction. (a), (b) 920ºC with annealing. (c), (d) 920ºC without annealing (e), (f) 940ºC without annealing. (g), (h) 970ºC without annealing.

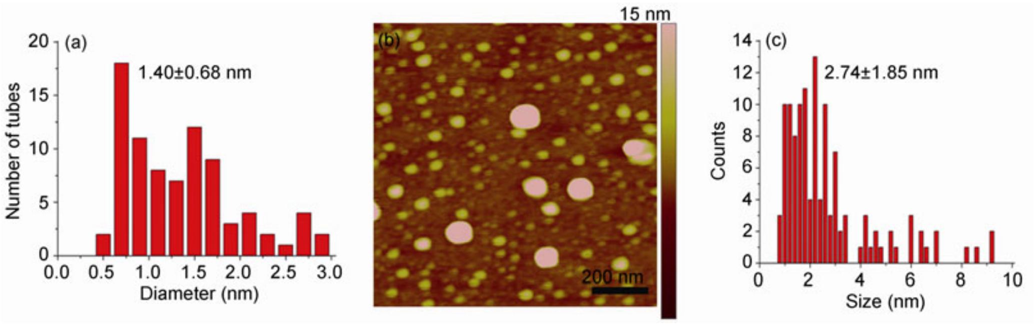

Figure 6 (a) Diameter distribution of SWNTs grown at 920°C using a mixture of Fe and Mo compounds as catalyst precursors. (b),(c) AFM image and size distribution of the mixture of Fe and Mo compounds after H_2 reduction at 920°C.

control experiment. We used the mixtures of $FeCl_3$ and $Mo(acac)_2$ with the same Fe/Mo ratio as that of the nanoclusters (1: 2.8) as the catalyst precursor and performed the CVD process under exactly the same growth procedure and condition as what had been done for Fe-Mo nanoclusters. Figure 6(a) shows the statistics of diameters of the resultant SWNTs grown at 920°C. The diameters vary from 0.5 to 3.0 nm with a mean value of 1.40 nm and a standard deviation of 0.68 nm. The average diameter is much larger than that of SWNTs from Fe-Mo nanoclusters and the diameter distribution is much broader. Then, what is the reason for the ununiformity of the SWNT diameters? We further checked the composition and the size of the Fe-Mo nanoparticles from the corresponding salts. The result of XPS measurements of the produced Fe-Mo nanoparticles was listed in Table 1. It seems that the composition of Fe-Mo nanoparticles prepared from the mixture of the corresponding salts is similar to those from the nanocluster precursors. However, the diameters are quite different. The sizes of the catalyst particles were checked by AFM after being reduced with H_2. Many large particles are found in the AFM image (Figure 6(b)) due to conglomeration. The average diameter is 2.74 nm with a standard deviation of 1.85 nm (Figure 6(c)). It is found that the diameter distribution of SWNTs is much narrower than that of the catalyst nanoparticles in the annealed case. The average diameter of the produced SWNTs is also much smaller than that of the nanoparticles. This attributes to the size-dependent activity of catalyst nanoparticles [32]. Because the larger nanoparticles need higher carbon feeding to get activated, so only smaller nanoparticles can initiate the growth of SWNTs under the relatively low carbon feeding at the modest growth temperature of 920°C. Therefore, SWNTs of smaller diameter and narrower diameter distribution were prepared. This control experiment shows that using Fe-Mo nanoclusters takes the advantage of forming uniform catalyst nanoparticles and that SWNTs with narrow diameter distribution can be obtained consequently.

From all above, our strategy to obtain SWNTs of small diameter and narrow size distribution includes four key points. First, using Fe-Mo nanoclusters of identical size as the catalyst precursors ensures the uniformity of the catalyst particle size; Second, the crystalline substrates exhibits further control over the diameter of the produced SWNTs; Third, using Ar atmosphere during the heating process prevents the formation of volatile MoO_3, which may cause the ununiformity of the catalyst particles; Forth, using ethanol instead of methane as the carbon feeding stocks benefits the tube growth at relatively lower temperatures.

3 Conclusions

In summary, we obtained aligned SWNTs with narrow diameter distribution on quartz substrates using identical molecular Fe-Mo nanoclusters as catalyst precursors. Such molecular nanoclusters formed uniform catalyst nanoparticles hence SWNTs of narrow diameter distribution were prepared. The sizes of the catalyst nanoparticles increased with the growth temperature. So did the diameters of the produced SWNTs. Low growth temperature was favorable for growing nanotubes with smaller diameters and narrow diameter distribution. At temperatures lower than 920°C, the average diameters of the SWNTs are below 1 nm, which is dramatically smaller than all previously reported results for aligned SWNTs. This can be attributed to the collaborative effect of using identical molecular nanoclusters as catalyst precursors and the size confinement of quartz substrates. By employing these kinds of molecular nanoclusters as catalyst precursors and carefully tuning the growth parameters, it is expected to realize the accurate control on the SWNT diameters, even obtaining SWNTs of designed structures.

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